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THEORY OF EXTRACTION

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"Several small extractions are better than one big one." Doubtless you've heard this many times, but now I'm going to try to show that it is true.

By way of example, let's say you have an *aqueous* solution of oxalic acid, and you need to isolate it from the water by doing an extraction. In your handbook, you find some solubilities of oxalic acid as follows: 9.5 g/100 g in water; 23.7 g/100 g in ethanol; 16.9 g/100 g in diethyl ether. Based on the solubilities, you decide to extract into ethanol from water, forgetting for the moment that ethanol is *soluble in water* and that you *must have two insoluble liquids* to carry out an extraction. Chagrined, you choose diethyl ether.

From the preceding solubility data we can calculate the **distribution**, or **partition coefficient** for oxalic acid in the water-ether extraction. This coefficient (number) is just the ratio of solubilities of the compound you wish to extract in the two layers. Here,

$$K_p = \frac{\text{solubility of oxalic acid in ether}}{\text{solubility of oxalic acid in water}}$$

which amounts to 16.9/9.5, or 1.779.

Imagine you have 40 g of oxalic acid in 1000 ml of water, and you put that in contact with 1000 ml of ether. The oxalic acid *distributes itself between the two layers*. How much is left in each layer? Well, if we let x g equal the amount that stays in the water, $1.779x$ g of the acid has to walk over to the ether. And so

$$\begin{aligned}\text{Wt of oxalic acid in ether} &= (1000 \text{ ml})(1.779x \text{ g/ml}) = 1779x \text{ g} \\ \text{Wt of oxalic acid in water} &= (1000 \text{ ml})(x \text{ g/ml}) = 1000x \text{ g}\end{aligned}$$

The total weight of the acid is 40 g (now partitioned between two layers) and

$$\begin{aligned}2779x \text{ g} &= 40 \text{ g} \\ x &= 0.0144\end{aligned}$$

and

$$\begin{aligned}\text{Wt of oxalic acid in ether} &= 1779 (0.0144) \text{ g} = 25.6 \text{ g} \\ \text{Wt of oxalic acid in water} &= 1000 (0.0144) \text{ g} = 14.4 \text{ g}\end{aligned}$$

Now, let's start with the same 40 g of oxalic acid in 1000 ml of water, but this time we will *do three extractions with 300 ml of ether*. The first 300 ml portion hits, and

$$\text{Wt of oxalic acid in ether} = (300 \text{ ml})(1.779x \text{ g/ml}) = 533.7x \text{ g}$$

$$\text{Wt of oxalic acid in water} = (1000 \text{ ml})(x \text{ g/ml}) = 1000x \text{ g}$$

The total weight of the acid is 40 g (now partitioned between two layers) and

$$1533.7x \text{ g} = 40\text{g}$$

$$x = 0.0261$$

and

$$\text{Wt of oxalic acid in ether} = 533.7 (0.0261)\text{g} = 13.9 \text{ g}$$

$$\text{Wt of oxalic acid in water} = 1000 (0.0261)\text{g} = 26.1 \text{ g}$$

That ether layer is removed, and the *second jolt* of 300 ml fresh ether hits, and

$$\text{Wt of oxalic acid in ether} = (300 \text{ ml})(1.779x \text{ g/ml}) = 533.7x \text{ g}$$

$$\text{Wt of oxalic acid in water} = (1000 \text{ ml})(x \text{ g/ml}) = 1000x \text{ g}$$

But here we started with 26.1 g of acid in water (now partitioned between two layers) and

$$1533.7x \text{ g} = 26.1\text{g}$$

$$x = 0.0170$$

and

$$\text{Wt of oxalic acid in ether} = 533.7 (0.0170)\text{g} = 9.1 \text{ g}$$

$$\text{Wt of oxalic acid in water} = 1000 (0.0170)\text{g} = 17.0 \text{ g}$$

Again, *that ether layer is removed*, and the *third jolt* of 300 ml fresh ether hits, and

$$\text{Wt of oxalic acid in ether} = (300 \text{ ml})(1.779x \text{ g/ml}) = 533.7x \text{ g}$$

$$\text{Wt of oxalic acid in water} = (1000 \text{ ml})(x \text{ g/ml}) = 1000x \text{ g}$$

But here, we started with 17.0 g of acid in water (now partitioned between two layers) and

$$1533.7x \text{ g} = 17.0 \text{ g}$$

$$x = 0.011$$

and

$$\text{Wt of oxalic acid in ether} = 533.7 (0.011) \text{ g} = 5.87 \text{ g}$$

$$\text{Wt of oxalic acid in water} = 1000 (0.011) \text{ g} = 11.0 \text{ g}$$

(They don't quite add up to 17.0 g—I've rounded them off a bit.)

Let's consolidate what we have. First, 13.9 g, then 8.5 g and, finally 5.34 g of oxalic acid, for a total of 27.7 g of acid extracted into 900 ml of ether. OK, that's not far from 24.7 g extracted *once* into 1000 ml of ether. That's because the distribution coefficient is fairly low. But it is *more*. That's because *several small extractions are better than one large one*.